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THE ROTATIONAL DIFFUSION OF PARA-AZOXY-ANISOLE MOLECULES IN LIQUID CRYSTAL AND ISOTROPIC LIQUID STATE

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ABSTRACT

Rotational diffusion motion of rod-like molecules are discussed. Inelastic incoherent neutron scattering measurements are presented and the rotational diffusion constant is determined from these data.

РЕЗЮМЕ

Рассматривается вращательное диффузионное движение стрежнеподобных молекул. Измерение неупругого некогерентного рассеяния нейтронов проведено и постоянная вращательной диффузии определяется из данных измерений.

KIVONAT

Ebben a cikkben pálca alaku molekulák rotációs diffuziós mozgását vizsgáljuk. Bemutatjuk a rugalmatlan neutronszórással kapott mérési eredményeinket. Ezekből meghatározzuk a molekulák rotációs diffuziós állandóját.

Keywords:
Liquid crystals
Neutron inelastic scattering
Rotational diffusion

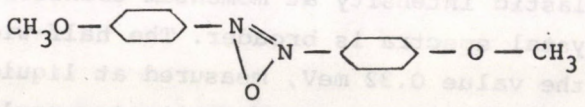
INTRODUCTION

In recent years considerable physical and technical interest has been paid to liquid crystals. Liquid crystals are characterized by the presence of an orientational order of rod-like molecules of which centres of gravity are completely disordered as in classical liquid. There is no satisfactory microscopic theory for this ordered state, and very little is known about the dynamic behaviour of molecules in such a system.

Bulkin [1], Blinc [2] , and Janik [3] have investigated the dynamic properties of such a system by Raman spectroscopy, NMR, and neutron methods. The techniques of investigation, and the methods and resolution of the present authors differ from these. In this article we are mainly concerned with inelastic incoherent cold neutron data of para-azoxy-anisole /PAA/ in solid, liquid crystal and isotropic liquid states.

I. EXPERIMENTAL

The chemical structure of PAA is



At a temperature range of 116° - 136°C PAA is in the liquid crystal state and has the coefficient of thermal expansion $0.72 \cdot 10^{-3}C^{-1}$ and dielectric anistoropy $\varepsilon_a = \varepsilon_{\parallel} - \varepsilon_{\perp} = -0.21$, i.e. negative. If the dielectric anisotropy of the system is negative the molecule can not be oriented by an electric field. In the sample of 0.5 - 1 mm thickness the turbulent motion of the molecule starts at rather small voltages /~50 V/. This effect /Williams domain, dynamic scattering/ is known [4] and was observed by polarizing microscope. The detailed investigation of the phenomena is published in [5].

The liquid crystal material used in this experiment was synthesized in the Chemical Department of our Institute.

The inelastic neutron scattering data observed at different temperatures 107°C; 118.5°C; 137°C and scattering angles 45°, 65°, 85°, 105° were measured with the stochastic time of flight spectrometer. This spectrometer is composed of a monochromator unit of a cold Be filter and Zn single crystal and an analysing unit of a stochastic neutron chopper and BF_3 detector. The intensity collection was made by 4 x 1028 channel KFKI analyser. The energy of the ingoing neutron beam was $E_o = 4.7 \pm 0.1$ meV, the time of flight base 5 m. The sample of area 10 cm^2 and thickness 1 mm was contained in an aluminium vessel, whose temperature was controlled to within 1°C.

II. RESULTS

a./ Liquid crystal state

The measured quasi-elastic neutron spectra are shown in Fig. 1. The dotted lines in the figure indicate the elastically scattered intensity in solid PAA. These agree with our ingoing neutron spectra. The solid lines at different scattering angles are the quasi-elastically scattered neutron intensities. The broadening of the quasi-elastic intensity compared to ingoing spectra can easily be seen. The angle i.e. the momentum transfer /Q/ dependence of the half-width values is shown in Fig. 2.

b./ Isotropic liquid state

The quasi-elastic intensity at momentum transfer $Q = 1.17\ \text{Å}^{-1}$ compared to liquid crystal spectra is broader. The half-width value of it is 0.43 MeV compared to the value 0.32 meV, measured at liquid crystal phase. The change of the spectra as a function of scattering angles or /Q/ is shown in Fig. 3.

III. THEORY

The PAA molecule contains hydrogen atoms therefore the scattering of neutrons is of an incoherent nature. This means that interference between the scattered waves from several molecules is absent. From such neutron data we can determine the motion of the individual molecule, the rotation and translation of a single molecule and the frequency spectrum.

Frenkel [6] has pointed out that in large molecules inside the translational, the rotational heat motion is important. The translational

diffusion i.e. the self-diffusion constant of similar molecules was measured by Blinc [7] and the value $D \approx 3.10^{-6}$ $cm^2 sec^{-1}$ was found. The rotational heat motion of such molecules can be written by different models.

a./ Rotational continuous diffusion model

In the case of substances with complex rod-shaped molecules the rotational motion preserves the character of small oscillation above the ordinary melting point i.e. in liquid crystal state, the molecules remain parallel to each other. The motion of the axis of molecules is described with the help of an ordinary diffusion equation in two dimensions

$$\frac{\partial G(r,t)}{\partial t} = D_r \left(\frac{\partial^2 G}{\partial x^2} + \frac{\partial^2 G}{\partial y^2} \right) = D_r \left[\left(\frac{1}{r} \frac{\partial}{\partial r} \frac{\partial G}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2 G}{\partial \rho^2} \right] \qquad /1/$$

where x,y are two rectangular axes in a plane tangentional to the corresponding portion of the spherical surface. Gdxdy is the number of molecula axes contained in a solid angle corresponding to the area dxdy and D_r is the coefficient of rotation diffusion. The solution of this equation is

$$G(r,t) = \frac{1}{t} e^{-\frac{r^2}{4D_r t}} \qquad /2/$$

The intermediate scattering function, the Fourier transfer in space of G(r,t) is

$$I(Q,t) = e^{-2Q^2 D_r t} \qquad /3/$$

and the scattering function

$$S(Q,\omega) = \frac{1}{\pi} \frac{Q^2 D_r}{(Q^2 D_r)^2 + \omega^2} \qquad /4/$$

is Lorentzian type with

$$\Delta E = 2hD_r Q^2 \qquad /5/$$

half-width value.

b./ Rotary motion in one dimension

The rotary motion of a molecule may be described as one-dimensional [8] if the motion of every point of the particle is a simple rotation about

a single axis, which passes through the centre of gravity of the molecule. Motions of this type may be described in terms of a single angle ϕ between the axis of molecule and a suitable reference axis in space. Both axes passing through the centre of gravity at right angles to the axis of rotation.

The rotation of the molecules will be one-dimensional if the particles are planar and lie parallel to a single plane. /This is probably the case in cholesteric state/.

A variable $\rho/\phi/$ is now introduced, such that the number of molecules in cm^3 with orientation between ϕ and $\phi + d\phi$ is $\rho/\phi/\, d\phi$. If there is not any spatial interaction between molecules which orient them in particular direction, $\rho/\phi/$ will then be a constant, independent of ϕ. If a certain orientation became more probable than another, $\rho/\phi/$ becomes dependent on ϕ. When orientational interaction is removed /e.g. in the region of phase transition to isotropic liquid state/, a gradual redistribution of orientation will occur. This process is known as rotary diffusion.

This process can be written by the rotary diffusion equation

$$\frac{\partial \rho\phi}{\partial t} = \theta_o \frac{\partial^2 \rho(\phi)}{\partial \phi^2} \qquad /6/$$

where θ_o is called the rotary diffusion coefficient. /Such types of motion are probably important in liquid crystals in the region of isotropic liquid phase transition where the orientational ordering is small or remains only in domains./ The correction between the rotary diffusion coefficient and the rotary frictional coefficient ζ is given by the equation

$$\theta_o = \frac{K_B T}{\zeta} \qquad /7/$$

The rotary frictional coefficients depend on the shape and size of the particle and on the location of the axis of rotation with respect to the axes of the molecule. In the case of a sphere of radius R,

$$\zeta = 8\pi\eta R^3. \qquad /8/$$

For a long prolate ellipsoid with semi-axes of length a and b, for rotation about one of the b axes Perrin [9] gives

$$\zeta = \frac{16\pi\eta a^3}{3\left[-1+2 \ln \frac{2a}{b}\right]} . \qquad /9/$$

For PAA $a \approx 9$ Å; $b \approx 3.4$ Å; $\eta = 0.02\text{-}0.03$ poise.
This formula gives a value $\theta_o \approx 10^8 - 10^9$ sec^{-1}.

c./ Spherical rotational diffusion model

The rotational diffusion for spherical molecules, or when the orientational distribution of molecular axes is given by the equation

$$D_r \left\{ \frac{1}{\sin\Theta} \frac{\partial}{\partial\theta}(\sin\Theta \frac{\partial}{\partial\Theta}) + \frac{1}{\sin^2\Theta} \frac{\partial^2}{\partial\rho^2} \right\} G(\omega_o,\omega,t) = \frac{\partial}{\partial t} G(\omega_o,\omega,t), \qquad /10/$$

was investigated by Sears [10] and the rotational correlation function

$$F_\ell(t) = (2\ell+1)\langle P_\ell(\cos\Theta(t)P_\ell(\cos\Theta(o)\rangle = e^{-\ell(\ell+1)Drt} \qquad /11/$$

was found, where P_ℓ is a Legendre polinomial and $\Theta/t/$ is the orientation of molecules at time with respect to an axis fixed in space. The scattering function is

$$S_R(\omega) = \frac{1}{\pi} \frac{\ell(\ell+1)\ D_r}{\omega^2+[\ell(\ell+1)D_r]^2} \qquad /12/$$

with $\Delta E = 2\hbar\ \ell(\ell+1)\ D_r$ halfwidth value. /13/

d./ Rotational jump diffusion model

In jump diffusion the molecular axis has a fixed average direction for the time τ and then jumps instantaneously to a new direction. Ivanov [11] has discussed this model and has arrived at the formula

$$F_\ell = e^{-(\Delta\omega)_\ell t} \quad , \qquad /14/$$

where

$$(\Delta\omega)_\ell = \frac{1}{\tau} \left[1 - (2\ell+1)^{-1} \int_0^\pi d\varepsilon W(\varepsilon) \frac{\sin(\ell+\frac{1}{2})\varepsilon}{\sin\frac{\varepsilon}{2}} \right] ; \qquad /15/$$

$W(\varepsilon)$ is the distribution of the jump steps of ε. The diffusive step is defined as the net angular movement made in the time τ.

$W(\varepsilon)$ is almost random distribution since

$$W(\varepsilon) \approx \sin\frac{\varepsilon}{2}\ e^{-\varepsilon/d_o} \cdot \frac{1}{2}\left(1 + \frac{4}{d_o^2}\right) \qquad /16/$$

where d_o is the average jump length.

Under this approximation, the half-width value of the scattering function is

$$\Delta E_\ell = \frac{\hbar \ell(\ell+1)\, D_r}{1+\ell(\ell+1)\, D_r \tau} \qquad /17/$$

e./ The collective librational motion

Chandrasekhar [12] and Kobayashi [13] have shown that in the ordered state the molecules undergo librational motion. This mode of motion has a collective nature, and in the molecular field approximation its frequency is

$$\omega = \sqrt{\frac{3\beta_o K_B TS}{2I}} \qquad /18/$$

where I is the moment of inertia, S is the orientational order parameter, β_o is a small quantity connected with the correlation length. In Kobayashi model the frequency spectrum was supposed to be Debye type, but this has not been proved experimentally.

IV. INVESTIGATION OF ROTATIONAL MOTION BY NEUTRON

The incoherent cross-section for the scattering of slow neutron by nuclei may be written in terms of an intermediate scattering function $I_s/Q,t/$ as follows

$$\frac{d^2\sigma}{d\Omega d\omega} = \sigma_{ink} \frac{K}{K_o} S(Q,\omega) = \sigma_{ink} \left(\frac{E}{E_o}\right)^{1/2} \frac{1}{2\pi} \int dt e^{-i\omega t} I_s(Q,t) \qquad /19/$$

where, for a classical system

$$I_s(Q,t) = \langle \exp\{i\, \bar{Q}|\bar{r}(t) - \bar{r}(0)|\}\rangle \qquad /20/$$

and $\langle \ldots\ldots \rangle$ denotes a thermal average, and $r(t)$ is the position vector of a proton at time t. $\hbar\omega = E-E_o$ is the energy transferred and $\hbar\theta = \hbar\,(K-K_o)$ is the momentum transferred on scattering. The $r(t)$ position vector of a proton at a time t may be written in a good approximation as the sum of the position vector for the centre of gravity $R(t)$ and of a proton's position $d(t)$, relative to the centre of gravity, ie.

$$\bar{r}(t) = \bar{R}(t) + \bar{d}(t).$$

In this case

$$I_s(Q,t) \approx \langle \exp\{i\bar{Q}|R(t) - R(0)|\}\rangle \langle \exp\{i\bar{Q}|d(t) - d(0)|\}\rangle =$$

$$= I_{nrot}(Q,t) \cdot I_r(Q,t) \ , \qquad /21/$$

where I_{nrot} includes all motions which are not rotations.

If vector $d(t)$ is of fixed magnitude for all the protons in the molecule /spherical molecule/ the second factor may be expanded as a double series of spherical harmonics.
Sears [10] points out that on averaging, the cross term vanishes and

$$I_r(Q,t) = \langle e^{i\bar{Q}|\bar{d}(t) - \bar{d}(0)|}\rangle = \sum_{\ell=0}^{\infty} (2\ell+1) j_\ell^2(Qd)\, F_\ell(t) \qquad /22/$$

where j_ℓ is a spherical Bessel function and $F_\ell(t)$ is the rotational correlation function /and has the form /11// .

$$\frac{d^2\sigma}{d\Omega\, d\omega} \propto \left(\frac{E}{E_o}\right)^{1/2} S_{\text{cent of gr}}(Q,\omega) \cdot S_R(Q,\omega) \qquad /23/$$

where

$$S_R(Q,\omega) \approx j_o^2(Qd)\, \delta(\omega) + \sum_{\ell=1}^{\infty} (2\ell+1) j_\ell^2(Qd)\, S_R(\omega) \qquad /24/$$

and

$$S_R(\omega) = \frac{1}{2\pi} \int dt\, e^{-i\omega t}\, F_\ell(t) \ ; \ F_o(t) = 1 \ . \qquad /25/$$

The half-width value of the cross-section with the simple rotational scattering function is shown in Fig. 3.

V. DISCUSSION

From the corrected time of flight spectra it is possible to make the following observations.

a./ The broadening of the quasi-elastic peak in Fig. 1 and 3 shows the change in molecular motion in solid, liquid crystal, and in isotropic liquid state.

b./ The broadening is strongly phase-dependent: in liquid crystal state only broadening, in the isotropic liquid state a split of the peak can, surprisingly, be seen.

c./ The momentum transfer dependence of the half-width in liquid crystal state /Fig. 2/ shows that with simple translational diffusion $\Delta E = 2\hbar Q^2 D$, we cannot interpret the broadening due to two reasons. First, the functional dependence is different, secondly, its value is larger.

d./ We cannot interpret the broadening even by a rotary diffusion model II.b, because the value of the model $\Theta \sim 10^8\text{-}10^9$ sec^{-1} is too small to be measured by neutrons, and the functional form is different.

e./ The functional form of the broadening is similar to the one calculated from the simple rotational diffusion model II.c. 11 and shown in Fig.2. The calculated rotational diffusion constant from our data has the value

$$D_r = (1{,}2 \pm 0{,}3)\ 10^{11}\ \text{sec}^{-1}.$$

The mentioned II.c. model is a spherically symmetric one. The material in principle is not. But in our sample the molecules were not oriented by rubbing the surface or by magnetic field. Therefore the orientational ordering was only in domains but not in the whole sample. These results show that it is worth measuring an oriented sample and to improve the model to a cylindrically symmetric one.

f./ In isotropic liquid state we cannot speak about simple broadening, because the quasi-elastic peaks split up into two satellite peaks at high Q values. The position of the satellite peaks seem to be constant, their intensity increases with Q^2. This we cannot interpret by simple rotational diffusion.

In isotropic liquid state orientational ordering destroys. The rotary motion of molecules from the preferred direction starts. The two peaks show that the motion of molecules can not be a continuous one. The basis of this motion is the jump motion, that is, the molecules make librational or small rotary motions for a time τ and then jump to a new direction. The motion during τ is a quantized one, the peaks are the loss and gain intensities. The scattering function of such a system can be written in the form

$$S_{\pm 1}(Q,\omega) = \frac{\hbar Q^2}{4\pi M} \int \frac{e^{+\frac{\hbar\nu}{2K_BT}}}{2\nu\ \text{sh}\ \frac{\hbar\nu}{2K_BT}}\, \rho(\nu)d\nu\ \frac{f(Q)}{f(Q)^2 + (\omega \pm \nu)^2}$$

where $f(Q) = D_r Q^2$ for simple rotational diffusion.

By studying the $\rho(\nu)d\nu$ frequency spectrum we can determine more. Is it Debye type as supposed by Kobayashi? The authors hope to answer this question in a future article.

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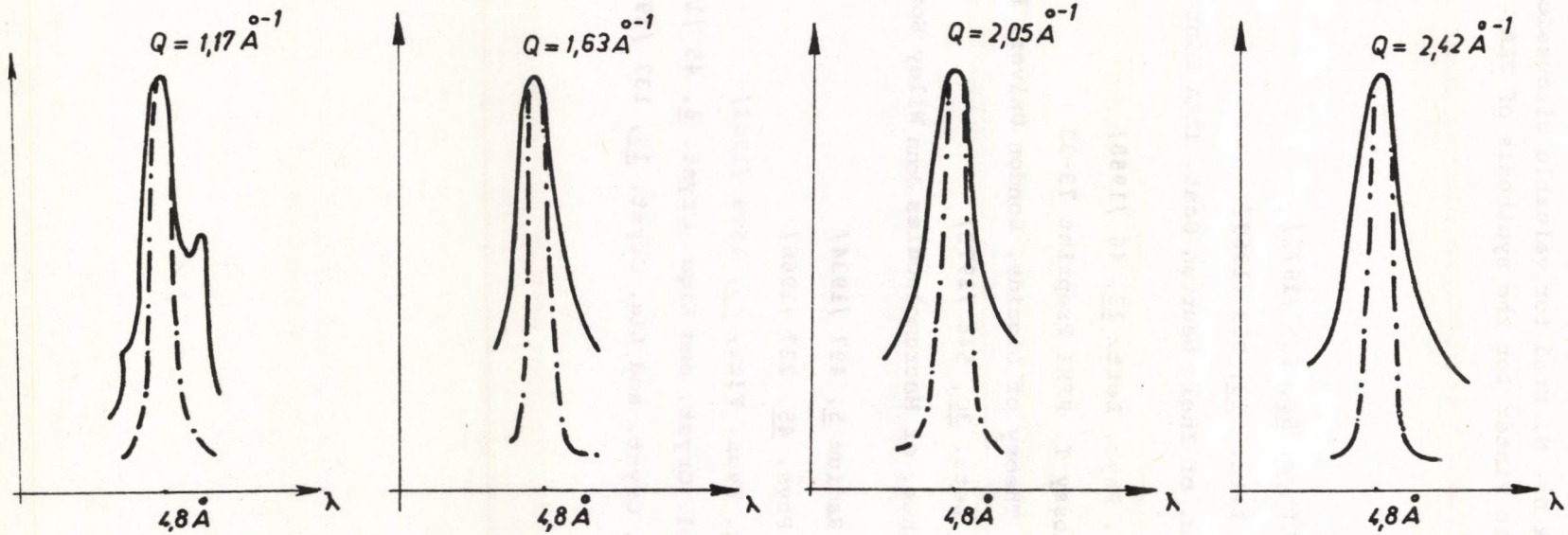

Fig. 1. Quasi-elastic neutron spectra for PAA at 118.5°C in liquid crystal phase. The dashed lines are the elastic neutron spectra measured at 107°C in solid phase

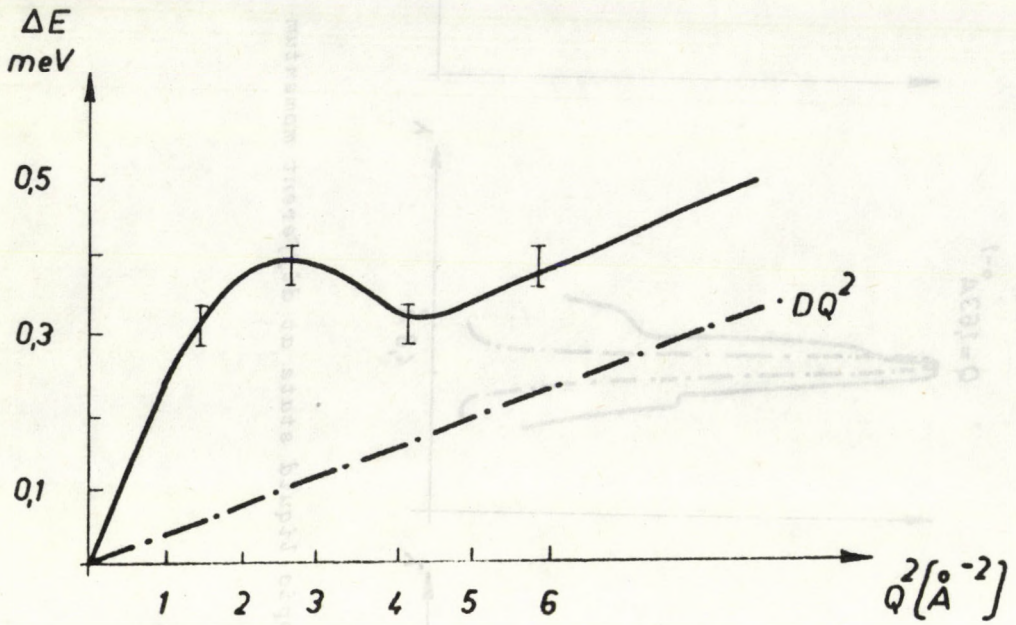

Fig. 2 *Broadening of the quasi-elastic intensities in liquid crystal state as a function of the square of the momentum transfer. The dotted line is the calculated broadening due to the translational diffusion with the constant* $D = 3.10^{-6}\ cm^2 sec^{-1}$

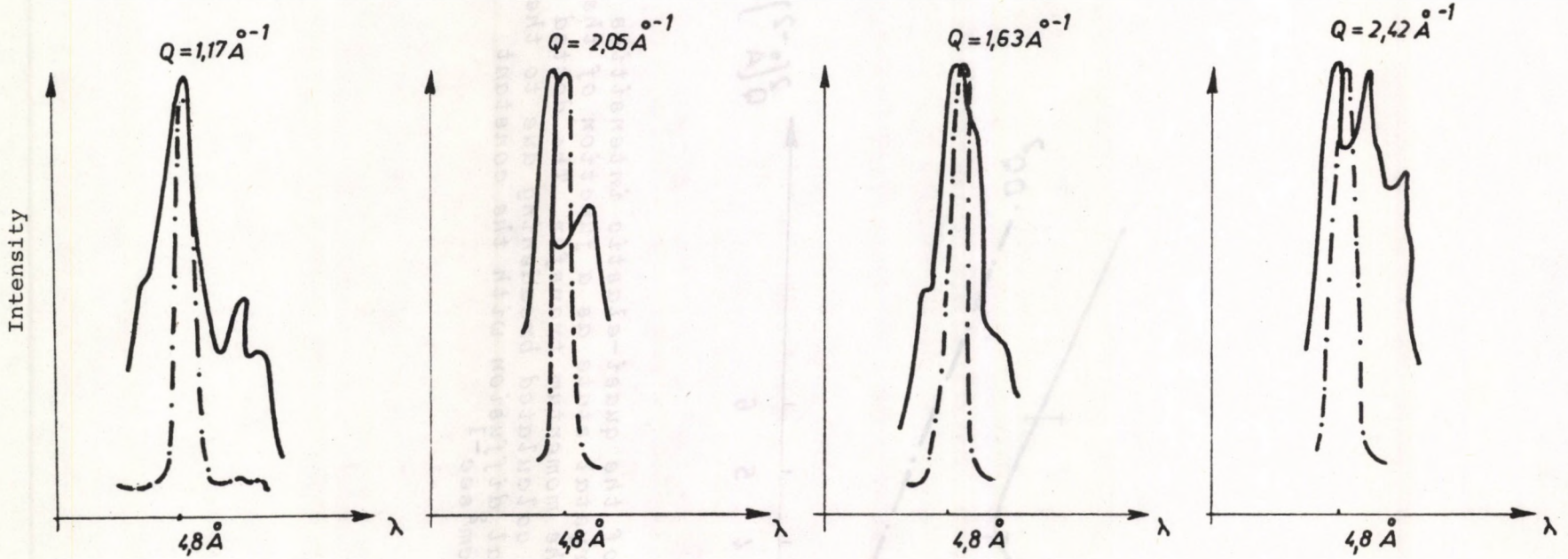

Fig. 3 *Quasi-elastic neutron spectra in isotropic liquid state at different momentum transfer*

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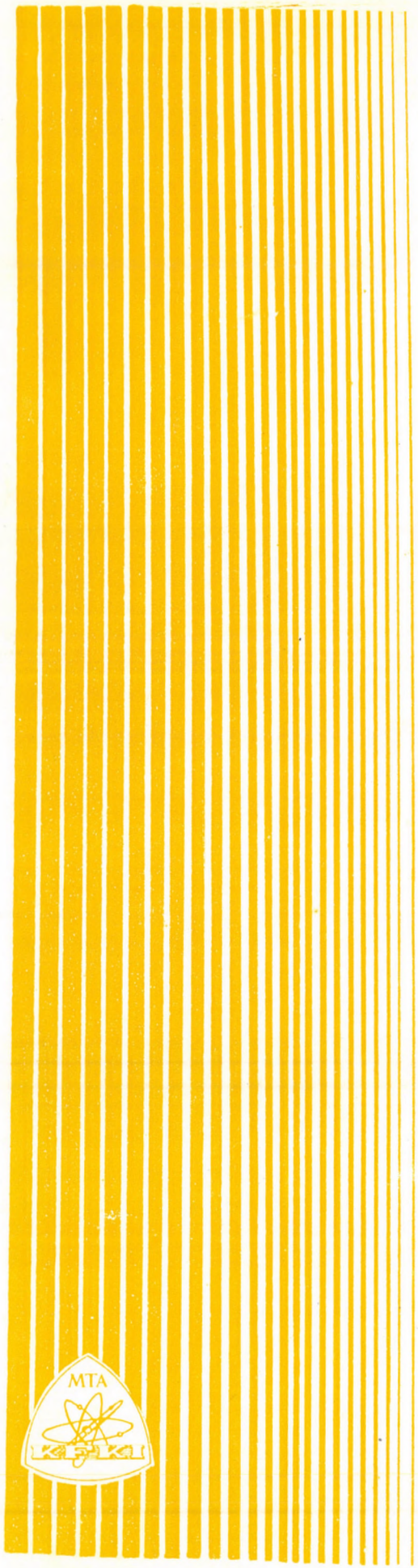

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